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<p>(21) International Application Number: PCT/FR98/00173 (22) International Filing Date: January 30, 1998 (1-30-98) (30) Information concerning Priority: 97/01049 January 31, 1997 (1-30-97) FR (71) Applicant (for all designated nations except the U.S.): RHODIA CHIMIE [FR/FR]; 25 quai Paul Doumer, F-92408, Courbevoie CEDEX (FR). (72) Inventors; and (75) Inventors/Applicants: (U.S. only): Vance BERGERON, [U.S./FR], 70-ter, rue Commandant Charcot, F-69005 Lyon (Fr). GUERIN, Giles [FR/FR]; 17, avenue Edouard Detaille, F-95600 Eaubonne (FR). (74) Agent: FABRE, Madeleine-France; Rhodia Services, Direction de la Propriété Industrielle, 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR)</p>		<p>(81) Designated Nations: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO Patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG) Published: <i>With international search report. Prior to expiration of the specified period for amending claims, the application shall be republished if amendments for claims are received.</i></p>
<p>(54) Title: A FOAM-PRODUCING AQUEOUS MEDIUM WHICH IS STABLE IN THE PRESENCE OF GREASE; STABILIZATION OF A FOAM-PRODUCING AQUEOUS MEDIUM BEING USED IN THE PRESENCE OF GREASE (57) Abstract A foam-producing aqueous medium which is capable of forming stable foams in the presence of grease and includes water, at least one basic surfactant which is capable of dispersing and/or dissolving grease within water, and at least one amphiphilic additive (ADD) which is compatible with said basic surfactant, wherein the amphiphilic additive shall provide surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m when the concentration of said amphiphilic additive within water is 0.1% by weight, and wherein it shall possess an affinity for grease which is less than the affinity of said basic surfactant for said grease. Stabilization of foam in the presence of grease within an aqueous medium containing at least one basic surfactant, by adding to said aqueous medium an amphiphilic additive which is compatible with said basic surfactant, wherein said amphiphilic additive (ADD) shall provide surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m when the level of said amphiphilic additive within water is 0.1 % by weight, and wherein it shall possess an affinity for grease which is less than the affinity of the basic surfactant for said grease. Use of said foam-producing aqueous medium as a liquid detergent composition for washing dishes or textiles by hand, or as a liquid composition for personal hygiene, oral hygiene, or body care.</p>		

A FOAM-PRODUCING AQUEOUS MEDIUM WHICH IS STABLE IN THE PRESENCE OF GREASE; STABILIZATION OF A FOAM-PRODUCING AQUEOUS MEDIUM BEING USED IN THE PRESENCE OF GREASE

The present invention pertains to a foam-producing aqueous medium which is capable of forming a foam which shall remain stable in the presence of grease, to stabilization of foam in the presence of grease by means of an amphiphilic additive, within an aqueous medium containing a basic surfactant, and likewise to use of said aqueous medium which is capable of producing foam which shall remain stable in the presence of grease as a liquid detergent composition for washing dishes by hand, as a liquid cosmetic composition for skin or hair, such as shampoos, shower gels, liquid soap, and as a composition for flotation of metals...

Different types of additives have been proposed within prior art for the purpose of stabilizing foams originating from aqueous media containing surfactants, especially within the field of detergents.

In "Additives for Foams," by KUO-YANN LAI and NAGARAJ DIXIT, in Foams Theory: Measurements and Applications, edited by Robert K. Prud'homme and Saad A. Khan, Surfactant Science Series, Marcel Dekker, Inc., 1955, Volume 57, Chapter 8, some of the organic compounds which are specifically cited include:

- Fatty alcohols, such as lauryl alcohol, for improving the stability of aqueous media containing anionic surfactants such as alkyl sulfates or alkylsulfonates or non-ionic surfactants such as ethoxylated alcohols;
- Alkanolamides such as lauryl monoethanolamide and lauryl isopropylamide in order to improve the stability of aqueous media containing anionic surfactants such as alkyl aryl-sulfonates;
- Amino oxides, such as N, N-dimethyldodecyl oxide or N,N-dimethylmyristyl amine, for improving the stability of aqueous media containing anionic surfactants such as alkyl ether sulfates and alkyl aryl sulfonates;
- Electrolytes, such as disodium acid phosphate, disodium pyrophosphate, and pentasodium triphosphate, for improving the stability of aqueous media which contain sodium laurate;
- Hydrophilic polymers, such as:
 - Non-ionic water-soluble derivatives of cellulose or guar gum, for improving the stability of aqueous media containing anionic surfactants such as alkyl sulfates, alkylether sulfonates or alkylsulfonates, or non-ionic surfactants such as ethoxylated alcohols or amphoteric substances such as betaines.

These various additives nonetheless possess the disadvantage of not always providing sufficient stability for foam which is formed in the presence of grease.

The Applicant has discovered a foam-producing aqueous medium whose foam offers significantly improved stability in the presence of grease.

One of the objects of the invention consists of a foam-producing aqueous medium which is capable of forming a stable foam in the presence of grease, with said foam-producing aqueous medium containing

water and at least one basic surfactant which is capable of dispersing and or dissolving grease within water, while being characterized by the fact that it also contains an amphiphilic additive which is compatible with said basic surfactant, while said amphiphilic additive (ADD), in a 0.1 % concentration by weight within water, provides surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m and preferably less than 22 mN/m at 25° C. and possesses a lower affinity for grease than the affinity of said basic surfactant for grease.

Grease is to be understood as any liquid and/or solid hydrophobic medium containing hydrocarbons which possesses water solubility of less than 5 g/l, and preferably less than 1 g/l.

The aforementioned grease may originate from the external environment, and/or it may be a component of the foam-producing aqueous medium itself. It may constitute either a hydrophobic form of contamination or an active hydrophobic compound within a detergent or cosmetic preparation, for example.

As examples of grease, it is possible to cite:

- Aliphatic or aromatic hydrocarbons (alkanes, paraffins, mineral oils, paraffin oils, kerosene, petroleum, fuel-oil, perhydrosqualane, squalene...)
- Alkylmonoglycerides, alkyl diglycerides, and triglycerides, such as oils extracted from plants and vegetables (palm oil, oils from copra, cottonseeds, soy, sunflowers, olives, grapeseed, sesame, peanuts, castor beans...) or oils of animal origin (tallow, fish oils...), derivatives of the aforementioned oils, such as hydrogenated oils, lanolin derivatives;
- Fatty alcohols, such as ketyl alcohol, stearyl alcohol, oleic alcohol;
- Fatty esters, such as isopropyl palmitate, ethyl-2-hexyl cocoate, myristyl myristate, esters of lactic acid, stearic acid, behenic acid, isostearic acid;
- Polyorganosiloxane oils, gums, or resins, such as linear or cyclic polydimethylsiloxanes, α - ω hydroxylated polydimethylsiloxanes, α - ω trimethylsilylated polydimethylsiloxanes, polyalkylmethylsiloxanes, polymethylphenylsiloxanes, polydiphenylsiloxanes, amino derivatives of silicones, silicone waxes;
- Organic contamination (sebum...)

Any types of non-ionic, anionic, amphoteric, zwitterionic, and cationic surfactants may constitute basic surfactants.

Among these surfactants, it is possible to cite:

- Anionic surfactants, such as:
 - Alkylester sulfonates with a $R-CH(SO_3M)-COOR'$ formula, where R represents a C_8-C_{20} radical and preferably a $C_{10}-C_{16}$ alkyl radical, where R' represents a C_1-C_6 alkyl radical and preferably a C_1-C_3 alkyl radical, and where M represents an alkaline cation (sodium, potassium, lithium), a substituted or unsubstituted ammonium ion (methylammonium, dimethylammonium, trimethylammonium, or tetramethylammonium, or dimethylpiperidinium...), or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine...);

- Alkylsulfates with a ROSO_3M formula, where R represents a $\text{C}_5\text{-C}_{24}$ alkyl or hydroxyalkyl radical and preferably a $\text{C}_{10}\text{-C}_{18}$ alkyl or hydroxyl radical, while M represents a hydrogen atom or a cation with the same definition as the preceding definition, as well as ethoxylated and/or propoxylated derivatives containing an average of 0.5 to 30 ethoxylated and/or propoxylated moieties, and preferably from 0.5 to 10 ethoxylated and/or propoxylated moieties;
- Alkylamide sulfates with a $\text{RCONHR}'\text{OSO}_3\text{M}$ formula, where R represents a $\text{C}_2\text{-C}_{22}$ alkyl radical and preferably a $\text{C}_6\text{-C}_{20}$ alkyl radical, while R' represents a $\text{C}_2\text{-C}_3$ alkyl radical, and M represents a hydrogen atom or a cation with the same definition as the preceding definition, as well as ethoxylated and/or propoxylated derivatives containing an average of 0.5 to 60 ethoxylated and/or propoxylated moieties;
- Salts of $\text{C}_8\text{-C}_{24}$, and preferably $\text{C}_{14}\text{-C}_{20}$ fatty acids which are saturated or unsaturated, $\text{C}_9\text{-C}_{20}$ alkylbenzene sulfonates, primary or secondary $\text{C}_8\text{-C}_{22}$ alkylsulfonates, alkylglycerol sulfonates, sulfonated polycarboxylic acids which are described within Patent GB-A 1, 082,179, paraffin sulfonates, n-acyl N-alkyltaurates, alkylphosphates, isethionates, alkylsuccinamates, alkylsulfosuccinates, sulfosuccinate monoesters or diesters, N-acyl sarcosinates, alkylglycoside sulfates, polyethoxycarboxylates, wherein the cation is an alkaline metal (sodium, potassium, lithium), a substituted or unsubstituted ammonium group (methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, dimethylpiperidinium...), or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine...)
- Sophorolipids, such as sophorolipids in an acidic or lactone form, derivatives of 17-hydroxyoctadecenic acid;

Non-ionic surfactants, such as:

- Polyoxyalkylenated (polyethoxyethylenated, polyoxypropylenated, polyoxybutylenated) alkylphenols, where the alkyl substitution group is a $\text{C}_6\text{-C}_{12}$ alkyl which contains from 5 to 25 oxyalkylene moieties. As examples, it is possible to cite *TRITON X-45*, *X-114*, *X-100*, or *X-102*, which are marketed by *Rohm & Haas Company*, and *IGEPAL NP2* to *NP17*, from *RHONE-POULENC*.
- Polyalkylenated $\text{C}_8\text{-C}_{22}$ aliphatic alcohols which contain from 1 to 25 oxyalkylene (oxyethylene, oxypropylene) moieties. As examples, it is possible to cite: *TERGITOL 15-S-9* and *TERGITOL 24-L-6 NMW*, which are marketed by *UNION CARBIDE CORP.*; *NEODOL 45-9*, *NEODOL 23-65*, *NEODOL 45-7*, and *NEODOL 45-4*, which are marketed by *Shell Chemical Company*, *KYRO EOB*, which is marketed by *The Procter & Gamble Company*, and *SYNPERONIC A3* to *A9*, *RHODASURF IT*, *DB*, and *B* from *Rhone-Poulenc*.
- Products obtained from condensation of ethylene oxide or propylene oxide with propylene glycol and ethylene glycol, whose molecular weight is approximately 2,000 to 10,000, such as the forms of *PLURONIC* which are marketed by *BASF*.
- Products obtained from condensation of ethylene oxide or propylene oxide with ethylene diamine, such as the forms of *TETRONIC* which are marketed by *BASF*.
- Ethoxylated and/or propoxylated $\text{C}_8\text{-C}_{18}$ fatty acids containing from 5 to 25 ethoxylated and/or propoxylated moieties;
- $\text{C}_8\text{-C}_{20}$ fatty acid amides which contain from 5 to 30 ethoxylated moieties;

- Ethoxylated amines containing from 5 to 30 ethoxylated moieties;
- Alkoxyated amidoamines containing from 1 to 50 and preferably from 1 to 25, or, more specifically, from 2 to 20 oxyalkylene moieties(preferably oxyethylene);
- Amine oxides, such as oxides of C₁₀-C₁₈ alkyl dimethylamines, and oxides of C₈-C₂₂ alkoxy ethyl dihydroxyethylamines;
- Alkoxyated terpene hydrocarbons such as ethoxylated and/or propoxylated α - or β -pinenes which contain from 1 to 30 oxyethylene and/or oxypropylene moieties;
- Alkylpolyglycosides which may be obtained by condensation (by acid catalysis, for example) of glucose with primary fatty alcohols (Patents: US-A-3 598 865; US-A-4 565 647; EP-A-132-043; EP-A 132 046...) containing a C₄-C₂₀ alkyl group, and preferably a C₈-C₁₈ alkyl group as well as an average number of glucose moieties which is on the order of 0.5 to 3, and preferably on the order of 1.1 to 1.8 per mole of alkylpolyglycoside (APG). In particular, it is possible to cite alkylpolyglycosides which contain:
 - *A C₈-C₁₄ alkyl group and an average of 1.4 glucose moieties per mole
 - *A C₁₂-C₁₄ alkyl group and an average of 1.4 glucose moieties per mole
 - *A C₈-C₁₄ alkyl group and an average of 1.5 glucose moieties per mole
 - *A C₈-C₁₀ alkyl group and an average of 1.6 glucose moieties per mole
- which are respectively marketed with the designations *GLUCOPON 600 EC*®, *GLUCOPON 600 CSUP*®, *GLUCOPON 650 EC*®, *GLUCOPON 225 CSUP*®, from *HENKEL*;
- Glucosamides such as lauryl-N-methylglucosamide;

Cationic surfactants, such as:

- Primary, secondary, or tertiary fatty amines (such as *ARMEEN 12*®, *ARMEEN 2C*®, *ARMEEN DM12D*®, and *ARMEENE M2HT*®, which are marketed by *ARMOUR*);
- Fatty diamines (such as *DUOMEEN C*®, *DUOMEEN CD*®, and *DUOMEEN T*®, which are marketed by *ARMOUR*);
- Acetates of primary or secondary fatty amines (such as *ARMAC C*®, *ARMAC 18D*®, and *ARMAC T*®, which are marketed by *ARMOUR*);
- Benzalkonium chlorides;
- Quaternary ammonium halides (alkyldimethylammonium halides);

Amphoteric and zwitterionnic surfactants, such as:

- Alkylbetaines, alkyldimethylbetaines, alkylamidopropyldimethylbetaines, alkylamidopropylbetaines, alkylamidopropyl-dimethylbetaines, alkyltrimethylsulfobetaines, imidazoline derivatives such as alkylamphoacetates, alkylamphodiacetates, alkylamphopropionates, alkylamphodipropionates, alkylsultaines, or alkylamidopropyl-hydroxysultaines, where the alkyl group contains from 6 to 20 carbon atoms, products obtained from condensation of fatty acids and protein hydrolysates, amphoteric derivatives of alkylpolyamines, such as *Amphionic XL*®, and *Mirataine H2C-HA*, which are marketed by *Rhone-Poulenc*, and *Ampholac 7T/X*® and *Ampholac 7C/X*®, which are marketed by *Berol Nobel*.

Amphiphilic additives for stabilizing foams may be foaming or non-foaming additives.

It is preferable for said amphiphilic additive to provide intrinsic production of foam in the presence of water.

The outcome of this situation is that an aqueous solution (deionized water) containing 0.1% of the aforementioned additive by weight shall provide an approximate initial foam height of at least 100 mm at 41° C., according to the Ross-Miles foaming test (ASTM-D 1173-53).

The aforementioned additive must possess an affinity for grease which is less strong than the respective basic surfactant's affinity for grease.

This condition is accomplished when adding said additive to an aqueous solution of a basic surfactant does not allow tension at the interface between grease and the aqueous solution of a basic surfactant to change by more than 5 mN/M, preferably by no more than 3 mN/m, and, more specifically, by no more than 1 mN/m.

This characteristic of a given additive may also be expressed in the following form:

$$|\gamma_1 - \gamma_2| \leq 5 \text{ mN/m}$$

- and preferably $|\gamma_1 - \gamma_2| \leq 3 \text{ mN/m}$, and, more specifically, $|\gamma_1 - \gamma_2| \leq 1 \text{ mN/m}$,
- with γ_1 representing interface tension between grease and an aqueous solution of a basic surfactant (in other words, a solution without an additive),
- while γ_2 represents interface tension between grease and a foam-producing aqueous medium (in other words, a solution containing an additive).

In addition, the amphiphilic additive should be compatible with the basic surfactant.

This situation means that the presence of the aforementioned additive shall not cause destabilization of a solution of a basic surfactant in water.

Destabilization of this kind could be caused by the presence of ionic charges within an additive which are the opposites of charges originating from the basic surfactant.

It is therefore advisable not to place a cationic additive in contact with a basic anionic surfactant within the aforementioned foam-producing aqueous medium, or vice versa.

On a wholly preferential basis, the aforementioned additive is a fluorinated compound.

Among fluorinated amphiphilic additives which may be used, it is possible to cite:

- Anionic, non-ionic, or amphoteric perfluoroalkylated surfactants which possess the previously indicated characteristics, such as:
- Agents whose formula is:

- * $\text{F}(\text{CF}_2\text{CF}_2)_{3-8}\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{COOLi}$
- * $\text{F}(\text{CF}_2\text{CF}_2)_{3-8}\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{H}$
- * $\text{F}(\text{CF}_2\text{CF}_2)_{3-8}\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{CH}_3\text{SO}_4^-$
- * $\text{F}(\text{CF}_2\text{CF}_2)_{3-8}\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CO}_2^-$

- which are marketed by *du Pont de Nemours* with the respective designations *ZONYL FSA*, *ZONYL FSO*, *ZONYL FSC*, and *ZONYL FSK*;

- Perfluoroalkyl betaines, such as the product which is marketed by *Elf-Atochem* with the designation *FORAFAC 1157*, ethoxylated polyfluoroalcohols, such as the product marketed by *Elf-Atochem* with the designation *FORAFAC 1110D*, and ammonium polyfluoroalkyl salts such as the product sold by *Elf-Atochem* with the designation *FORAFAC 1179*;

- Surfactants whose hydrophilic portion includes one or more saccharide moieties containing from five to six carbon atoms (formations derived from sugars such as fructose, glucose, mannose, galactose, talose, gulose, allose, altose, idose, arabinose, xylose, lyxose, and/or ribose) and whose hydrophobic portion contains a moiety with a $\text{R}_\text{F}(\text{CH}_2)_n$ -group, where n may vary from 2 to 20, and preferably from 2 to 10, while R_F represents a perfluoroalkyl group with the formula $\text{C}_m\text{F}_{2m+1}$, where m may vary from 1 to 10 and preferably from 4 to 8, with the respective moiety being selected among those which possess the previously defined characteristics. It is also possible to cite monoesters of perfluoroalkylated fatty acids and sugars such as α,α -trehalose and sucrose, where the monoester function may be represented by the formula $\text{R}_\text{F}(\text{CH}_2)_n\text{C}(\text{O})$, where n may vary from 2 to 10 and where R_F represents a perfluoroalkyl formation with the formula $\text{C}_m\text{F}_{2m+1}$, where m may vary from 4 to 8, as described within *JAOCs*, Volume 69, Number 1 (January, 1992), with said monoesters being selected among those which possess the previously defined characteristics.

- Polyelectrolytes containing fatty perfluoroalkyl side groups, such as polyacrylates containing $\text{R}_\text{F}(\text{CH}_2)_n$ -groups, where n may vary from 2 to 20 and preferably from 2 to 10, while R_F represents a perfluoroalkyl moiety with the formula $\text{C}_m\text{F}_{2m+1}$, where m may vary from 1 to 10 and preferably from 4 to 8, with selection according to polyacrylates possessing the previously defined characteristics. It is possible to cite polyacrylates containing $-\text{CH}_2\text{C}_7\text{F}_{15}$ groups which are described within *J. Chim. Phys.* (1996), 93, 887-898 and are to be selected among those which possess the previously defined characteristics.

Respective amounts of different components of the aforementioned foam-producing aqueous medium are such that this foam-producing aqueous medium shall contain an amount of the basic surfactant on the order of 0.1 to 10 g/l, preferably on the order of 0.3 to 5 g/l, and more specifically on the order of 0.3 to 1.5 g/l, expressed as dry material, with the weight ratio between the amphiphilic additive and the basic surfactant being on the order of 0.5/100 to 40/100 and preferably on the order of 0.5/100 to 30/100 when it is expressed in terms of dry material.

The aforementioned foam-producing aqueous medium can be prepared by a simple procedure involving mixing of the different ingredients according to any order.

Another object of the present invention consists of using at least one amphiphilic additive which is compatible with the respective basic surfactant within an aqueous medium containing at least one surfactant which is capable of dispersing and/or dissolving grease within water, whereby said amphiphilic additive (ADD), in a concentration of 0.1% by weight within water, shall provide surface tension, $\lambda_{(\text{ADD})/\text{water/air}}$ which is less than 25 mN/m and preferably less than 22 mN/m at 25° C. and shall possess less affinity for grease than the affinity of the respective basic surfactant for said grease.

The nature and relative quantities of the basic surfactant and of the amphiphilic additive which are to be present within the aforementioned aqueous medium have been indicated previously.

A third object of the invention consists of a method of stabilizing foam in the presence of grease within an aqueous medium containing at least one basic surfactant by adding to said aqueous medium an amphiphilic additive (ADD) which is compatible with the aforementioned basic surfactant, with said amphiphilic additive providing surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m and preferably less than 22 mN/m at 25 ° C. while possessing less affinity for the grease than the affinity of the respective basic surfactant for said grease.

The presence of an amphiphilic additive within a foam-producing aqueous medium allows foaming performance levels (according to the test described within the example) which are at least equal to 20% and preferably at least equal to 80%, to be obtained for a weight ratio below 40 and preferably below 10 between grease and the basic surfactant + an amphiphilic additive.

The aforementioned foam-producing aqueous medium to which the invention pertains, which is capable of forming stable foams in the presence of grease, can be used in various applications requiring use of a foam-producing medium which possesses sufficient stability in the presence of grease.

The aforementioned foam-producing aqueous medium can be used as a liquid detergent composition for washing dishes or textiles by hand. In addition, it can contain other customary ingredients for this type of application, such as:

- Bactericidal agents or disinfectants, such as trichlosan;
- Synthetic cationic polymers such as *MIRAPOL A550®* and *MIRAPOL A15®*, which are marketed by *RHONE-POULENC*, or *MERQUAT 550®*, which is marketed by *CALGON*.
- Polymers which are used to regulate the viscosity of the respective mixture and/or the stability of foam formed during use, such as cellulose or guar derivatives (carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylguar, carboxymethylguar, carboxymethylhydroxypropylguar...)
- Hydrotropic agents, such as simple C₂-C₈ alcohols, notably ethanol, diols, and glycols, such as diethylene glycol, dipropyleneglycol...
- Hydrating or moisturizing agents for the skin, such as glycerol or urea, or skin protecting agents such as proteins or protein hydrolysates, cationic polymers such as cationic guar derivatives (*JAGUAR C13S®*, *JAGUAR C162®*, and *HICARE 1000®*, which are marketed by *RHONE-POULENC*);
- Dyes, fragrances, preservation agents...
- Enzymes;
- Agents which bind iron and bivalent ions (especially calcium and magnesium), such as aminocarboxylates, including, for example, ethylenediamine tetraacetates, nitrilotriacetates, and aminophosphonates, such as nitrilo-3 (methylene phosphonates), water-soluble salts of polycarboxylic acids with molecular weights on the order of 2,000 to 100,000, which are obtained by polymerizing or copolymerizing carboxylic acids without ethylene saturation, such as acrylic acid, maleic acid or maleic anhydride, fumaric acid, itaconic acid, aconitic acid, citraconic acid, methylenemalononic acid, and specially polyacrylates whose molecular weight is on the order of 2,000

to 10,000 (Patent US-A-3-308-067), acrylic acid copolymers and maleic anhydride with a molecular weight on the order of 5,000 to 75,000 (Patent EP-A-66 915).

The aforementioned medium can also be used as a liquid composition for bodily hygiene, oral hygiene, or body treatments (skin and hair), such as shampoos, shower gels, liquid soaps, shaving creams, depilatory creams..., and it may also contain other customary ingredients for these types of applications.

Within the areas of hygiene or skin and hair treatments, the aforementioned aqueous medium may also contain:

- Additional vehicles, such as ethanol, volatile silicones (such as phenyl pentamethylsiloxane, methoxypropyl heptamethylcyclotetrasiloxane, chloropropyl pentamethyldisiloxane, hydropropyl pentamethyldisiloxane, octamethyl cyclotetrasiloxane, decamethylcyclopentasiloxane, cyclodimethicone, and dimethicone);
- Propellants such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane, or isobutane;
- Conditioning agents (which improve the attributes of hair in terms of combing, hair-dressing, tactile quality, and volume), including conditioning agents of animal origin, such as hydrolyses of animal proteins, including ammonium salts of dimethyl stearate or trimethyl stearate, and collagen, silk, and keratin hydrolysates; conditioning agents of synthetic origin, which are usually known as polyquaternium, such as the copolymer of N,N'-bis (dimethylamino)-3 propyl)urea and oxy-1, 1'-bis(chloro-2) ethane, or polyquaternium-2; copolymers of diallyldimethyl ammonium chloride and acrylamide or polyquaternium-7; cationic polysaccharide derivatives, such as cocodimonium hydroxyethyl cellulose, hydroxypropyltrimonium chloride guar, hydroxypropyl guar, hydroxypropyl trimonium chloride (*JAGUAR C13S*, and *JAGUAR C162*, which are marketed by *RHONE-POULENC*), poly(oxyethanediyl-1,2)ether, trimethylammonium-3-propyl cellulose hydroxy-2 chloride, or polyquaternium-10; silicone derivatives, such as amodimethicone, cyclomethicone, ketyl dimethicone copolyol, cyclomethicone, dimethicone copolyol, trimethylsilyl amodimethicone, polyquaternium-80; surfactants of the cationic type, such as ammonium polyalkyl halides, including, for example ammonium distearyl dimethyl chloride;
- Emollients such as alkylmonoglycerides, alkyl diglycerides, and triglycerides such as oils extracted from plants and vegetables (palm, copra, cottonseed, soy, sunflower, olive, grapeseed, sesame, peanut, and castor bean oils...), or oils of animal origin (tallow, fish oils...), derivatives of these oils, such as hydrogenated oils, lanolin derivatives, mineral oils or paraffin oils, perhydrosqualane, squalene, diols such as 1-2-propanediol, 1-3-butanediol, ketyl alcohol, stearic alcohol, oleic alcohol, polyethyleneglycols or polypropyleneglycols, fatty esters such as isopropyl palmitate, ethyl-2-hexyl cocoate, myristyl myristate, esters of lactic acid, stearic acid, behenic acid, isostearic acid, silicone oils which include cyclic polydimethylsiloxanes, hydroxylated α - ω polydimethylsiloxanes, trimethylsilylated α - ω polydimethylsiloxanes, and polyorganosiloxanes, such as polyalkylmethylsiloxanes, polymethylphenylsiloxanes, polydiphenylsiloxanes, amino derivatives of silicones, silicone waxes, copolyether silicones (such as *SILBIOINE 70646* oil, which is marketed by the *RHONE POULENC* Company, or *DC 190* which is marketed by *DOW CORNING*), or combined silicone derivatives which include different types of derivative formation (such as combined polyalkylmethylsiloxane-silicone copolyether copolymers).
- Moisturizing or hydrating agents such as carbohydrates (glycerol or sorbitol, for example), polyethylene glycols, or polypropylene glycols, alcoxylated sugar derivatives or their derivatives (methyl glucose for example), urea, gelatin, aloe vera, hyaluronic acid...

- Protective agents, such as polymer derivatives within the category of cellulose derivatives, such as cellulose hydroxyethers, methylcellulose, ethylcellulose, hydroxypropyl methylcellulose, hydroxybutyl methylcellulose, polyvinyl esters attached to polyalkylene stems, such as polyvinyl acetates attached to polyoxyethylene stems (Patent: EP-A-219 048), polyvinyl alcohols, copolyesters derived from acids, anhydrides, or terephthalic, and/or isophthalic, and/or sulfophthalic diesters and a diol, ethoxylated monoamines or polyamines, polymers of ethoxylated amines (Patents: US-A-4 597 898, EP-A-11 984).
- Plasticizers such as adipates, phthalates, isophthalates, azelates, stearates, silicone copolyols, glycols, castor oil, or mixtures thereof;
- Sequestration agents for metals, and more specifically those which sequester calcium, such as citrate ions;
- Polymeric dispersants for controlling hardness in calcium and magnesium, agents such as water-soluble salts of polycarboxylic acids with molecular weights on the order of 2,000 to 100,000, which are to be obtained by polymerization or copolymerization of carboxylic acids without ethylene saturation, such as acrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, methylene-malonic acid, and, most specifically, polyacrylates with a molecular weight on the order of 2,000 to 10,000 (Patent: US-A-3 308,067), acrylic acid and maleic anhydride copolymers with a molecular weight on the order of 5,000 to 75,000 (Patent: EP-A-66 915), and polyethyleneglycols with a molecular weight on the order of 1,000 to 50,000.
- Viscose-forming or gel-forming polymers such as reticulated polyacrylates (*CARBOPOL*, sold by *GOODRICH*), cellulose derivatives such as hydroxypropylcellulose, carboxymethylcellulose, guar, and their derivatives, xanthan gum...
- Sun screens, such as zinc oxide, titanium dioxide, or cerium oxides in the form of powders or colloidal particles;
- Preservation agents, fragrances, dyes...

Within the area of oral hygiene (toothpaste), the aforementioned aqueous medium may contain:

- Fluorinated compounds such as monofluorophosphoric acid salts;
- Moistening agents such as glycerol, sorbitol, polyethyleneglycols, lactitol, xylitol...
- Thickening agents, such as certain types of silica used for this purpose (*TILOSIL 43®*, marketed by *RHONE-POULENC...*) and/or polymers which are used alone or in combination with xanthan gum, guar gum, cellulose derivatives (carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose...), reticulated polyacrylates such as the forms of *CARBOPOL®* distributed by *GOODRICH*, alginates or carrageenan, *VISCARIN®*....
- Polishing abrasives, such as certain types of silica, precipitated calcium carbonate, magnesium carbonate, calcium phosphates, titanium, zinc, and stannous oxides, talc, kaolin...
- Therapeutic bactericidal, antimicrobial, and anti-plaque agents, such as zinc citrate, polyphosphates, guanidines, bis-biguanides, or other cationic therapeutic organic compounds;
- Scenting agents (essence of anise, badiane, mint, juniper, cinnamon, cloves, roses), sweeteners, dyes (chlorophyll), preservation agents...

The following example is provided as an illustration of the invention.

Example:

Raw materials to be used:

Basic Surfactant

- SDS: sodium dodecylsulfate, marketed by *FLUKA*.
 - C₁₄TAB: tetradecyltrimethylammonium bromide, marketed by *ALDRICH*.
 - FTAB: surfactant formulation containing:
 - 21% sodium lauryl ether sulfate (*EMPICOL ESB/3M*, marketed by *ALBRIGHT & WILSON*), according to dry weight
 - 3% ethoxylated alcohol containing an average of six oxyethylene moieties (*RHODASURF IDO60*, marketed by *RHONE-POULENC*), according to dry weight.
 - 3% cocoamidopropyl betaine (*DEHYTON K*, marketed by *HENKEL*), according to dry weight.
- q.s.p. 100% water, by weight.
- with adjustment of the pH to 7.

Grease:

50/50 mixture of sunflower oil and margarine, according to weight.

Additive:

- FORAFAC 1110D, ethoxylated polyfluoroalcohol marketed by Elf-Atochem.
- FORAFAC 1157, betaine perfluoroalkyl marketed by Elf-Atochem.
- FORAFAC 1179, polyfluoroalkyl ammonium salt marketed by Elf-Atochem.
- ZONYL FSK, with a $F(CF_2CF_2)_{3-8}CH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CH_2CO_2^-$ formula, which is marketed by du Pont de Nemours.

Performance of additives as stabilizing agents for foams was tested according to the following series of procedures:

250 ml of an aqueous solution containing 0.4% by weight of a surfactant or surface-active formulations such as *SDS*, *C₁₄TAB*, or *FTAB* were prepared.

1) The solution was placed inside a 2-liter beaker containing a stirrer with an anchor which was immersed halfway into this solution.

The solution was stirred at 400 r.p.m.'s for one minute.

The height of the foam (HM) was measured.

2) The previously described procedure (1) was repeated, and 10 ml of grease were added to the basic surface-active solution.

The medium was stirred at 400 r.p.m.'s for one minute.

The height of the foam (GHM) was measured.

3) The previously described procedure (1) was repeated, and 110 ml of grease and 0.1% additive by weight were added to the basic surface-active solution.
The medium was stirred at 400 r.p.m.'s for one minute.
The height of the foam (AGHM) was measured.

Performance of the additive (ADD) being tested is expressed by the following ratio:

$$P\% = [(AGHM - GHM) / GHM] \times 100$$

The results which were obtained appear within Table 1.

This table also includes the following measurements for solutions containing 0.4% SDS and C_{14} TAB as basic surfactants:

Water/air surface tension:

* $\gamma_{\text{water/air}}$ without an additive

* $\gamma_{\text{additive water/air}}$ in the presence of an additive (0.1%)

Grease/water interface tension:

* γ_1 , without an additive;

γ_2 , in the presence of an additive (0.1%).

Water/grease interface tension measurements were performed according to the drip method described within A.W. Adamson's text, *Physical Chemistry of Surfaces*, 2nd edition, New York, Interscience, 1967. Surface tension measurements were performed by means of a LAUDA® TVT1 tension meter.

It was observed that:

- Surface tension, $\gamma_{\text{additive water/air}}$, within aqueous solutions containing 0.1% additive were less than 22 mN/m.
- Addition of an additive to an aqueous solution containing a basic surfactant does not alter the surface tension for grease and an aqueous solution of a basic surfactant by more than 0.4 mN/m.

Table 1

ADDITIVE	Basic Surfactant <i>SDS</i>	Basic Surfactant <i>C₁₄TAB</i>	Basic Surfactant <i>FTAB</i>
None			
Height of foam (mm)	110	95	85
Height of foam with Grease (mm)	17	17	4
$\gamma_{\text{water/air}}$ (mN/m)	38.1	38.5	
γ_1 (mN/m)	6.3	9	
<i>FORAFAC 1110D</i>			
Height of foam with grease and additive (mm)	25	40	13
P%	47%	135%	225%
$\gamma_{\text{additive water/air}}$ (mN/m)	18.3	18.1	
γ_2 (mN/m)	6.5	9	
$ \gamma_1 - \gamma_2 $ (mN/m)	0.2	0	
<i>FORAFAC 1157</i>			
Height of foam with grease and additive (mm)	50	60	23
P%	194%	253%	475%
$\gamma_{\text{additive water/air}}$ (mN/m)	16.4	15.8	
γ_2 (mN/m)	5.9	8.6	
$ \gamma_1 - \gamma_2 $ (mN/m)	0.4	0.4	
<i>FORAFAC 1179</i>			
Height of foam with grease and additive (mm)	25	75	5
P%	47%	341%	25%
<i>ZONYL FSK</i>			
Height of foam with grease and additive (mm)	36	65	
P%	112%	282%	

CLAIMS

- 1) A foam-producing aqueous medium which is capable of forming stable foams in the presence of grease, with said foam-producing aqueous medium consisting of water and a basic surfactant which is capable of dispersing and/or dissolving grease within water, characterized by the fact that it also contains an amphiphilic additive (ADD) which is compatible with said basic surfactant, and wherein said amphiphilic additive, according to a 0.1% concentration by weight within water, shall provide surface tension, $\gamma_{(\text{ADD}) \text{ water/air}}$, which is less than 25 mN/m and is preferably less than 22 mN/m at 25° C., while displaying an affinity for grease which is less than the basic surfactant's affinity for said grease.
- 2) A foam-producing aqueous medium according to Claim 1, characterized by the fact that said basic surfactant is non-ionic, anionic, amphoteric, zwitterionic, or cationic.
- 3) A foam-producing aqueous medium according to Claims 1 or 2, characterized by the fact that the aforementioned amphiphilic additive is intrinsically capable of producing foam in the presence of water.

- 4) A foam-producing aqueous medium according to any of the Claims identified as 1 to 3, characterized by the fact that said amphiphilic additive is of such a nature that its being added to an aqueous solution containing a basic surfactant does not allow modification of the interface tension between grease and the aqueous solution of a basic surfactant by more than 5 mN/m, preferably by no more than 3 mN/M, and, most specifically, by no more than 1 mn/M.
- 5) A foam-producing aqueous medium according to Claim 3 or 4, characterized by the fact that the aforementioned additive shall be a fluorinated compound.
- 6) A foam-producing aqueous medium according to Claim 5, characterized by the fact that the aforementioned additive is an anionic, non-ionic, or amphoteric perfluoroalkylated surfactant, or a polyelectrolyte containing fatty perfluoroalkyl side groups.
- 7) A foam-producing aqueous medium according to Claim 6, characterized by the fact that the aforementioned additive is to be selected among:
- Surfactants with the following formulas:
 $*F(CF_2CF_2)_{3-8}CH_2CH_2SCH_2CH_2COOLi$
 $*F(CF_2CF_2)_{3-8}CH_2CH_2O(CH_2CH_2O)_yH$
 $*F(CF_2CF_2)_{3-8}CH_2CH_2SCH_2CH_2N+(CH_3)_3CH_3SO_4^-$
 $*F(CF_2CF_2)_{3-8}CH_2CH(OCOCH_3)CH_2N+(CH_3)_2CH_2CO_2CO_2^-$
 - Perfluoroalkyl betaines;
 - Ethoxylated polyfluoroalcohols;
 - Ammonium polyfluoroalkyl salts;
 - Surfactants whose hydrophilic portion shall include one or more saccharide moieties containing from five to six carbon atoms and whose hydrophobic portions shall include moieties whose formula is $R_F(CH_2)_n-$, where n may vary from 2 to 20 and preferably from 2 to 10, while R_F represents a perfluoroalkyl moiety whose formula is C_mF_{2m+1} and where m may vary from 1 to 10 and preferably from 4 to 8;
 - Polyacrylates containing $R_F(CH_2)_n-$ groups where n may vary from 2 to 20 and preferably from 2 to 10, while R_F represents a perfluoroalkyl moiety whose formula is C_mF_{2m+1} and where m may vary from 1 to 10 and preferably from 4 to 8;
- 8) A foam-producing aqueous medium according to any of the claims identified as 1 to 7, characterized by the fact that respective amounts of different components of said foam-producing aqueous medium shall be such that the foam-producing aqueous medium shall include on the order of 0.1 to 10 g/l of the basic surfactant, expressed in terms of dry materials, preferably on the order of 0.3 to 5 g/l, and, more specifically, on the order of 0.3 to 1.5 g/l, with the weight ratio between the amphiphilic additive and the basic surfactant being on the order of 0.5/100 to 40/100 and preferably on the order of 0.5/100 to 30/100 when it is expressed in terms of dry materials.
- 9) Use of at least one amphiphilic additive which is compatible with a basic surfactant within an aqueous medium containing at least one basic surfactant which is capable of dispersing and/or dissolving grease within water, with said amphiphilic additive (ADD) providing surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m and preferably less than 22 mN/m at 25° C., when its concentration is 0.1% by weight within water, and possessing less affinity for grease than the affinity of said surfactant for said grease.
- 10) Use according to Claim 9, characterized by the fact that the respective basic surfactant is non-ionic, anionic, amphoteric, zwitterionic, or cationic.
- 11) Use according to Claim 9 or Claim 10, characterized by the fact that the amphiphilic additive is to be selected among those which are present within a foam-producing aqueous medium described within any of the claims identified as 3 to 7.

- 12) Use according to any of the Claims identified as 9 to 11, characterized by the fact that the respective amounts of basic surfactants and amphiphilic additives shall be of such a nature that the final foam-producing aqueous medium which is formed shall include a basic surfactant on the order of 0.1 to 10 g/l, preferably on the order of 0.3 to 5 g/l, and more specifically on the order of 0.3 to 1.5 g/l, expressed according to dry materials, with the weight ratio between the amphiphilic additive and the basic surfactant being on the order of 0.5/100 to 40/100, and preferably on the order of 0.5/100 to 30/100 when it is expressed according to dry materials.
- 13) A method for stabilizing foam in the presence of grease within an aqueous medium containing at least one basic surfactant, by adding to said aqueous medium an amphiphilic additive which is compatible with said basic surfactant, with said amphiphilic additive (ADD) in a concentration of 0.1% by weight within water providing surface tension, $\lambda_{(ADD)/water/air}$, which is less than 25 mN/m and preferably less than 22 mN/m at 25°C, while possessing an affinity for grease which is less than the affinity of said basic surfactant for said grease.
- 14) A method according to Claim 13, characterized by the fact that said basic surfactant is non-ionic, anionic, amphoteric, zwitterionic, or cationic.
- 15) A method according to Claim 13 or 14, characterized by the fact that the aforementioned amphiphilic additive is to be selected among those which are present within a foam-producing aqueous medium to which any of the Claims identified as 3 to 7 may pertain.
- 16) A method according to any of the Claims identified as 13 to 15, characterized by the fact that the respective quantities of basic surfactants and amphiphilic additives shall be of such a nature that the final foam-producing aqueous medium which is formed shall include a basic surfactant on the order of 0.1 to 10 g/l, preferably on the order of 0.3 to 5 g/l, and more specifically on the order of 0.3 to 1.5 g/l, expressed according to dry materials, with the weight ratio between said amphiphilic additive and said basic surfactant being on the order of 0.5/100 to 40/100, and preferably on the order of 0.5/100 to 30/100 when this ratio is expressed according to dry materials.
- 17) Use of a foam-producing aqueous medium to which any of the Claims identified as 1 to 8 pertain, as a liquid detergent composition for washing dishes by hand or textiles by hand.
- 18) Use of a foam-producing aqueous medium to which any of the claims identified as 1 to 8 pertain, as a liquid composition for personal hygiene, oral hygiene, or body care.